

ATTORNEY'S DOCKET NUMBER

9052-106

U S APPLICATION NO (If known, see 37 CFR 1.5)

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

10/049779

INTERNATIONAL APPLICATION NO.
PCT/GB00/03194

INTERNATIONAL FILING DATE
August 18, 2000

PRIORITY DATE CLAIMED
August 18, 1999

TITLE OF INVENTION

PROCESS FOR SEPARATING METALS

APPLICANT(S) FOR DO/EO/US

Robert Charles THIED, Justine Elizabeth HATTER, Kenneth Richard SEDDON, William Robert PITNER, David William ROONEY, and David HEBDITCH

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☐ Amendments to the claims of the International Application Under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired
 - d. ☐ have not been made, and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report Under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98, Form PTO 1449 and ____ references.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1 821 - 1.825.
18. ☒ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4)
20. ☒ Other items or information: PCT International Search Report (attached to published international application)

U.S. APPLICATION NO. (if known) 10/049779		INTERNATIONAL APPLICATION NO PCT/GB00/03194		ATTORNEY DOCKET NO 9052-106	
21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a) (1) - (5)).				CALCULATIONS PTO USE ONLY	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO				\$1040.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or IPO				\$890.00	
International preliminary examination fee 37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO				\$740.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)				\$710.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)				\$100.00	
ENTER APPROPRIATE BASE FEE AMOUNT =				\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e))				\$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	18 - 20 =	0	x \$18.00	\$	
Independent Claims	1 - 3 =		x \$84.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00	
TOTAL OF ABOVE CALCULATIONS =				\$	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2				\$	
SUBTOTAL =				\$	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f))				\$	
TOTAL NATIONAL FEE =				\$	
Fee for Recording the enclosed assignment (37 CFR 1.21(h)) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$890.00	
				Amount to be refunded:	\$
				charged:	\$

- a. ☒ A check in the amount of **\$890.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. 50-0220 in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0220. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



20792

PATENT TRADEMARK OFFICE

Laura M. Kelley
 Laura M. Kelley, Reg No 48,441
 Date: Feb. 18, 2002

CERTIFICATE OF EXPRESS MAILING

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Susan E. Freedman
 Susan E. Freedman

Attorney's Docket No. 9052-106

PATENT

IN THE UNITED STATES DESIGNATED OFFICE (DO/US)

In re: Application of Thied et al.
Serial No.: To be Assigned
Filed: Concurrently Herewith
For: ***PROCESS FOR SEPARATING METALS***

February 18, 2002

BOX PCT
Commissioner for Patents
Washington, DC 20231
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PRELIMINARY AMENDMENT

Sir:

Prior to the examination of the above application and calculation of claim fees, please amend the above-identified application as follows. Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The marked-up version of the changes to the claims is captioned "**Version With Markings To Show Changes Made.**"

In the Specification:

On page 1, line 1 after the title of the invention, please insert the following section:

--CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority under 35 U.S.C. § 371 from PCT Application No. PCT/GB00/03194 (published under PCT Article 21(2) in English), filed on August 18, 2000 which claims the benefit of Great Britain Application Serial No. 9919496.1, filed on August 18, 1999, the disclosures of which are incorporated by reference herein in their entireties.--

On page 3, line 10, delete the word "STATEMENTS" and insert --SUMMARY-- therefor.

In re: Application of Tried et al.
 Serial No.: To be assigned
 Filed: Concurrently herewith
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On page 13, line 1, delete the word "**CLAIMS**" and insert the following: --WHAT IS CLAIMED IS:--

In the Claims:

Please enter the amended claims as follows:

2. (Amended) A method according to claim 1 wherein the ionic liquid comprises a cation component.

3. (Amended) A method according to claim 2 wherein the cation component comprises an organic cation.

5. (Amended) A method according to claim 1 wherein the anode is selected from a group consisting of halide, nitrate, sulphate, tetrafluoroborate, hexafluorophosphate and tetrachloroaluminate.

6. (Amended) A method according to claim 1 wherein the anode comprises trifluoromethanesulfonate bis(trifluoromethanesulfonyl)imide.

7. (Amended) A method according to claim 1 wherein the ionic liquid is pre-loaded with metal ions.

10. (Amended) A method according to claim 9 wherein the metal chloride comprises AgCl or CdCl₂.

12. (Amended) A method according to claim 1 further comprising depositing purified metal at the cathode.

13. (Amended) A method according to claim 1 further comprising depositing the metal at the cathode as a compound.

22. (New) A method according to claim 3 wherein the organic cation is selected from a group consisting of N-substituted pyridinium, N,N'-disubstituted imidazolium, tetraalkylammonium or tetraalkylphosphonium.

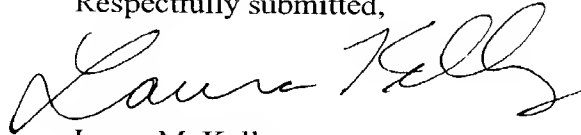
In re: Application of Tried et al.
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REMARKS

Applicant respectfully requests consideration of the foregoing amendments. The above claims have been amended to better conform to U.S. practice and to eliminate the multiple dependency of claims.

Please enter this amendment prior to calculating the fee in this case. Applicant respectfully requests substantive examination on the merits.

Respectfully submitted,



Laura M. Kelley
Registration No. 48,441

Correspondence Address:



20792

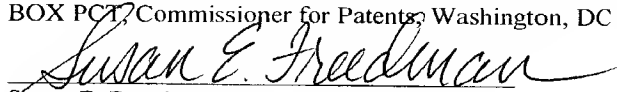
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Susan E. Freedman

Date of Signature February 18, 2002

In re: Application of Tried et al.
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Version With Markings To Show Changes Made

In the Specification:

On page 1, line 1 after the title of the invention, the following section has been added:

--CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority under 35 U.S.C. § 371 from PCT Application No. PCT/GB00/03194 (published under PCT Article 21(2) in English), filed on August 18, 2000 which claims the benefit of Great Britain Application Serial No. 9919496.1, filed on August 18, 1999, the disclosures of which are incorporated by reference herein in their entireties.--

In the Claims:

The claims have been amended as follows:

2. (Amended) A method according to claim 1 wherein [the cation component of] the ionic liquid comprises a cation component [is an organic cation].

3. (Amended) A method according to claim 2 wherein the cation component comprises an organic cation [is N-substituted pyridinium, N,N'-disubstituted imidazolium, tetraalkylammonium or tetraalkylphosphonium].

5. (Amended) A method according to [any of the preceding claims] claim 1 wherein the [anion component is] anode is selected from a group consisting of halide, nitrate, sulphate, tetrafluoroborate, hexafluorophosphate [or] and tetrachloroaluminate.

6. (Amended) A method according to [any claims 1 to 4] claim 1 wherein the [anion component is] anode comprises trifluoromethanesulfonate bis(trifluoromethanesulfonyl)imide.

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7. (Amended) A method according to [any of the preceding claims] claim 1 wherein the ionic liquid is pre-loaded with metal ions.

10. (Amended) A method according to claim 9 wherein the metal chloride [is] comprises AgCl or CdCl₂.

12. (Amended) A method according to [any of the preceding claims wherein] claim 1 further comprising depositing purified metal [is deposited] at the cathode.

13. (Amended) A method according to [any of the preceding claims wherein] claim 1 further comprising depositing the metal [is deposited] at the cathode as a compound.

14. (Amended) A method according to [any of the preceding claims] claim 1, wherein the composition to be separated is irradiated nuclear fuel.

15. (Amended) A method according to [any of the preceding claims] claim 1, wherein the metal to be separated [is] comprises uranium [and/or plutonium].

16. (Amended) A method according to [any of the preceding claims wherein, after use in the method, the ionic liquid is purified for further use] claim 1 further comprising purifying the ionic liquid for further use.

Claims 17-20 have been canceled.

Claims 21 and 22 have been added.

21. (New) A method according to claim 1 wherein the metal to be separated comprises plutonium.

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22. (New) A method according to claim 3 wherein the organic cation is selected from a group consisting of N-substituted pyridinium, N,N'-disubstituted imidazolium, tetraalkylammonium or tetraalkylphosphonium.

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PROCESS FOR SEPARATING METALS**FIELD OF THE INVENTION**

This invention relates to processes for the separation of metals from compositions
5 containing metals. The invention includes processes for the treatment of spent
nuclear fuel forming part of a process for reprocessing, conditioning and/or
partitioning nuclear fuels. Reference will be made hereinafter mainly to nuclear fuels
but it should be understood that the invention is not restricted to any particular type
of material and has application outside the nuclear industry.

10

BACKGROUND OF THE INVENTION

In the metals recovery and refining industry generally, the type of metal recoverable
from a solvent is dependent upon the size of the electrochemical window of the
solvent in which the metal is dissolved, and from which purification and recovery is
15 taking place. In aqueous solutions, this is governed by the electrochemical window
of water or supporting electrolyte. This limits the recovery, purification and
electroplating of metals on to surfaces from aqueous solution to those metals whose
electrode reduction potentials are more positive than the cathodic limit of the
aqueous solution. In acidic aqueous solution, metal ions would not be recoverable
20 where their electrode reduction potentials are more negative than that of the H_3O^+
ION. Recovery of metals with electrode reduction potentials more negative than
 H_3O^+ , means that non-aqueous (aprotic) solvents are required. There are a number of
aprotic solvents which are used. There are a number of non-protic solvents which are
used. These are often molten salts and, for instance, aluminium is industrially
25 purified electrochemically by electrolysis of Al_2O_3 dissolved in molten cryolite
 Na_3AlF_6 . Other aprotic media include the organic solvents, such as acetonitrile,
benzene and toluene.

There exists two well developed processes which use molten salts for the
30 reprocessing of irradiated nuclear fuel. The Argonne National Laboratory
electrometallurgical treatment (ANL - EMT) process and the Dimitrovgrad State

Scientific Centre, Research Institute of Atomic Reactors (SSC – RIAR) process both use molten salts at high temperatures (773 and 1000K respectively). The ANL process treats the spent nuclear fuel by a process called electrowinning in which current flow is used to oxidise a uranium anode to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as uranium metal. The SSC – RIAR process uses chemical oxidants (chlorine and oxygen gases) to react with powdered UO_2 fuel to form higher oxidation state compounds such as UO_2Cl_2 which are soluble in the molten salt. At the cathode the uranium compounds are reduced to UO_2 , which forms a dendritic deposit.

The disadvantage of these processes is that these molten salts are typically mixtures of salts which are liquid only at high temperatures and this causes inherent disadvantages in a reprocessing plant, in particular, as a result of the challenges posed in the engineering of the process and the materials of construction.

Ionic liquids free of molecular solvents were first disclosed by Hurley and Wier in a series of US patents (24446331, 2446339, 2446350). In general terms an ionic liquid is a salt, a mixture of salts, or a mixture of components which produce a salt or a mixture of salts, which melts below or just above room temperature. (As used herein, the term "salt" means an entity comprising entirely of cationic and anionic species). Such liquids are known as "ionic liquids" although this term is sometimes used for salts which melt at relatively high temperatures. In this specification, the term "ionic liquid" refers to a salt which melts at a temperature of up to 100°C .

Co-pending patent application PCT/GB99/00246 discloses a method for reprocessing spent nuclear fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid to substantially separate fissile material from other components of irradiated fuel. Also disclosed is the subsequent treatment of the resulting ionic liquor, either by solvent extraction or electrochemical treatment to recover the dissolved uranium and plutonium.

preferred, linear groups being preferred). Alternatively, the cation might be a substituted tetraalkylammonium or tetraalkylphosphonium ion, where the alkyl groups take the form of C_nH_{2n+1} for $1 \leq n \leq 6$, and are linear or branched groups. Preferred examples include tetrabutylammonium and tetrabutylphosphonium.

5 However, the alkyl groups are preferably of different lengths resulting in asymmetrical substitution. Alternatively, the cation might be a substituted pyridinium ion, where the substituent group also takes the form C_nH_{2n+1} for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups; suitable substituents include butyl, 2-(2-methyl)propyl, 2-butyl and octyl but straight chain alkyl, especially butyl,

10 is preferred.

The ionic liquid may be a mixture of two or more ionic liquids, which together provide the desired properties such as, for instance, a lower viscosity. An example is a mixture of disubstituted imidazolium in which the components of the mixture have

15 alkyl groups of different lengths, e.g. a mix of 1-octyl-3-methylimidazolium chloride ([cmim]Cl) and 1-ethyl-3-methylimidazolium chloride ([omim]Cl).

The anion component is likely to be an inorganic species such as halide (for instance, chloride), nitrate, sulphate, tetrafluoroborate, hexafluorophosphate or

20 tetrachloroaluminate, triflate which is trifluoromethanesulfonate ($CF_3SO_3^-$), and bistriflylimide which is bis(trifluoromethanesulfonyl)imide ($[(CF_3SO_2)_2N]^-$).

Preferably the ionic liquid will be pre-loaded with metal ions, in order that the electrorefining process can be initiated. Such pre-loading may be achieved by, for

25 example, the addition to the ionic liquid of a soluble uranium salt or a salt such as cadmium chloride. Addition of a metal salt, such as cadmium chloride, results in the reaction of this metal salt with uranium metal, creating metal ions in the solution.

Pre-loading with uranium ions may also be achieved by displacement of a metal

30 chloride, such as AgCl or $CdCl_2$. Alternatively, pre-loading with uranium ions may be achieved by destructive reduction of the electrolyte. At the anode uranium is

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oxidised to a soluble uranium species and, within a cathode compartment separated from the bulk of the solution, the organic cation of the ionic liquid or sacrificial organic reagent added to it, is destroyed.

- 5 The process can be applied to a variety of metal fuel feeds. Preferably the metal composition to be treated is irradiated nuclear fuel and the metal to be separated is uranium. Uranium or a uranium compound will be deposited at the cathode in a purified form. By changing the potential at the cathode, or by adding a second cathode to the system, it is possible to achieve separation and deposition of partly
10 purified plutonium.

By contrast with a process involving chemical dissolution, in an electrochemical process there can be much greater selectivity of the species to be dissolved. The potential at the anode can be controlled, such that metals which are more
15 electropositive than uranium, and with larger negative Gibbs free energies associated with the species formed in solution, are the only metals which dissolve at the anode. This is the first separation step, as many of the more noble metals will remain behind in an anodic sludge. The ionic liquid now contains a solution of metal ions including uranium and those of more electropositive species. A suitable potential is applied at
20 the cathode, whereby uranium and metals less electropositive than uranium are electrodeposited. This should only include uranium, as those less electropositive metals have not been anodically dissolved.

DETAILED DESCRIPTION OF THE INVENTION

- 25 If oxide fuels are to be treated there will probably be a need for a pre-treatment step, such as that performed in the ANL Lithium reduction process, to reduce the oxide fuel and form a metal feed. The metal fuel may also undergo a decladding process. This could take a number of forms such as mechanical removal or chemical dissolution of the cladding.

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In a preferred embodiment of the invention irradiated nuclear fuel feed in the form of metal is placed within an anode basket. The anode basket is then immersed within an ionic liquid, together with a suitable cathode, such as a stainless steel mandrel. Through the application of a suitable potential difference between the anode and
5 cathode, uranium metal will be electrochemically oxidised at the anode, and enter into the ionic liquid electrolyte medium. The soluble uranium species will then be electro-transported to the cathode, where a reduction process occurs. Contaminants with more positive reduction potentials than uranium will remain unoxidised in the anode basket. Similarly, contaminants with more negative reduction potentials than
10 uranium will remain unreduced in solution.

Electro-reduction of the soluble uranium species should result in the deposition of uranium metal (or a uranium compound) at the cathode. Provided that a suitable oxidising potential is applied at the anode and a suitable reduction potential is
15 applied at the cathode, uranium or a uranium compound will be deposited at the cathode in a purified form.

The ionic liquid contains fission product compounds and compounds of the actinide elements which are oxidised from the cathode with the uranium and must be stripped
20 of these contaminants before its subsequent re-use. This may be achieved by any one or a combination of a number of different routes. Selected fission products and actinides such as plutonium can be electrochemically extracted through the application of a suitable potential using a liquid metal cathode such as a mercury electrode. Alternatively, dissolved plutonium may be co-deposited on the cathode
25 with the uranium, irrespective of whether the metals are deposited in the metallic state (in the (0) oxidation state), as complexes or as oxides. Such co-deposition is useful in the manufacture of mixed oxide fuels.

Selective deposition of a metal from a solution containing its ions is well known in
30 the art and does not require detailed explanation here. However all metal ions in a solution will have different electrode reduction potentials to reduce the ions to a

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lower positive valency, or to reduce them to zero valency. Electrode reduction potentials are dependent upon the element, the oxidation state of the ion in the solvent and to the presence of other ions or molecules. If a potential is applied across a solution then all metal ions with a more positive potential will be deposited on the cathode. Metal ions with a more negative potential will remain in solution. Once a particular ion has been removed from the solution, the electrode can be removed and replaced with a new one, biased at a slightly more negative potential, for the deposition of the next metal with a more negative reduction potential. If it is desired to deposit two metals together, then a potential more negative than the reduction potential for both ions is applied.

Certain organic cations are selected for the ionic liquid, to give extremely low reduction potentials. The lower the "cathodic window" of the solvent, the greater the range of species which can be removed from solution by electroreduction. For example, imidazolium cations give at least a 1 volt advantage over aqueous solutions.

Fission products may alternatively or additionally be removed from the ionic liquid by the addition of an organic solvent. Addition of an organic species results in the precipitation of fission product compounds. The precipitate can be filtered from the ionic liquid and calcined to convert to oxide prior to a vitrification step. Cleaned ionic liquid can then be recycled to the electrorefiner.

In order to maximise process rate the electro-refining equipment is engineered to minimise anode to cathode distance and the cathode deposit is removed and collected. The latter step also prevents electrical shorting between the anode and cathode due to the growth of metallic dendrites.

The invention will now be further described with reference to the following examples. In each case the reference electrode was immersed in a 0.1 Molar solution of silver nitrate in [bmim] NO₃, separated from the bulk solution in a glass tube with a porous Vycor tip.

Example 1: anodisation of a uranium electrode in [bmim]NO₃ at room temperature

An electrochemical cell was set up with a separated platinum coil counter electrode, a Ag reference electrode, a uranium metal plate working electrode and [bmim]NO₃ (1-butyl-3-methylimidazolium nitrate) as electrolyte. Electrolysis was carried out by applying a potential of +0.6V to the uranium electrode. After the passage of 1000 Coulombs, the uranium electrode was removed and weighed. The weight loss of the uranium (0.78g) indicated that the uranium species required 3.2 equivalents per mole, indicating the production of a U(III) species.

10

Example 2: electrorefining uranium in [heim]Cl at 70°C

Due to the viscosity of [heim]Cl 1-hexyl-3-ethylimidazolium nitrate chloride, this work was carried out at 70°C. A solution of U(III) was produced in [heim]Cl as by electrolysis of a uranium electrode at +0.3 V. This is anodic dissolution of the uranium metal, as in Example 1. Comparison of the charge passed (1235 Coulombs) with the weight loss of the uranium electrode (1.012 g) gives a charge to mass balance of 3.0 eqv/mol, indicating the production of a U(III) species. The platinum counter electrode used in the preparation of this solution was then replaced with a copper wire immersed in the U(III) solution. Electrolysis was carried out at an applied potential of -1.6 V to the copper cathode; the uranium metal electrode served as the anode. A total of 236 Coulombs was passed during the electrolysis. The weight gain of the cathode electrode was only 18.7 mg compared to the 193 mg weight loss of the uranium anode. This clearly shows that uranium has been electrotransported from the anode to the cathode, the current efficiency being only about 10%. Material which settled on the bottom of the cell indicated that deposited uranium does not adhere well to copper. The charge to mass loss of the uranium electrode (236 C/193 mg = 3.0 eqv/mol) indicated that even while acting as a counter electrode, the species produced through anodisation is still U(III).

25

Example 3: voltammetry of U(III) in [emim]Cl at 80°C

7.99g [emim] Cl was melted at 80°C. A solution containing 0.03mol L⁻¹ (U(III)) was produced by the anodiation of a uranium rod (Q¹111C) as in Example 1. Cyclic voltammograms were recorded in the resulting solution at a glassy carbon electrode.

- 5 A typical voltammogram is shown in Figure 1. The oxidation of U(III) to U(IV) occurs at potentials greater than *ca.* -0.2V versus Ag(I)/Ag. This process is irreversible, as demonstrated by the large difference in the anodic and cathodic potentials (-0.06 and -1.07 V, respectively). The reduction of U(III) to U metal occurs at potentials less than *ca.* -1.5V.

10

This example thus shows the potential at which uranium (III) is reduced to metal, and shows that uranium can be purified from other metals, such as plutonium, by an electrochemical means.

15 Example 4: anodiation of Pu(III) in [emim]Cl at 90°C

An electrochemical cell was set up with a separated platinum coil counterelectrode, a Ag reference electrode, and a plutonium metal rod working electrode. Electrolysis was carried out by applying a potential of -1.5V to the plutonium electrode. After the passage of 27.5C, the plutonium electrode was removed and weighed. A direct
20 comparison of the weight loss of the plutonium (80mg) with the charge passed would erroneously indicate that the plutonium species generated was Pu(II). However, it was noted that plutonium metal in contact with the ionic liquid reacts spontaneously; the bright metal quickly forms a dark layer of corrosion products as the metal undergoes oxidation and the ionic liquid cation undergoes reduction. This is most
25 likely because the reduction potential of Pu(III) is more negative than that of the 1-ethyl-3-methylimidazolium cation (*ca.* -2.2V). Therefore, given the known chemistry of plutonium in chloride media, it is most likely that the species generated during electrolysis is Pu(III); the excess weight loss is due to spontaneous corrosion.

- 30 This example shows evidence that plutonium can anodically dissolve into an ionic liquid, and that the oxidation state is probably Pu(III).

The spontaneous corrosion of the plutonium is not necessarily a process issue, as when the basket contents are under electrotransport conditions, electrons are passed round the circuit to the cathode, rather than passing to the cations of the ionic liquid.

5

Example 5: voltammetry of Pu(III) in [emim]Cl at 90°C

Cyclic voltammograms were recorded at a glassy carbon electrode in the Pu(III) solution produced by anodisation of Pu(III) in [emim]Cl described in Example 4. A typical voltammogram is shown in Figure 2. The oxidation of Pu(III) to Pu(IV) occurs at potentials greater than *ca.* -0.2V. The Pu(IV)/Pu(III) redox couple is quasi-reversible with $\Delta E_p \approx 90\text{mV}$ ($E_p^a = -0.15\text{V}$, $E_p^c = -0.24\text{V}$). From the voltammogram, it is clear that reduction of Pu(III) to generate the metal does not occur at potentials greater than -2.2V, the cathodic limit of the ionic liquid below which potential the cation is reduced. A comparison of the potential windows of [bmim] [NO₃], [emim]Cl and LiCl-KCl eutectic is shown in Figure 3, which also graphically displays the potentials of various redox couples of plutonium and uranium in [emim]Cl at 90°C from Example 3 and Example 5. It should be clear from this graphic that the electrodeposition of uranium without the simultaneous deposition of plutonium is possible in the [emim]Cl ionic liquid at 90°C, allowing separation of uranium from plutonium.

20

This graphic shows that the electrochemical window of [emim]Cl at 90° is sufficiently wide that the reduction of U(III) to uranium metal can be performed within the ionic liquid, but is insufficiently wide for this to be the case with plutonium. Hence purification of uranium from plutonium is possible.

25

Use of a liquid metal electrode, such as mercury, may shift the electrode reduction potential of plutonium, so that it can too be electrodeposited at the liquid cathode. As an alternative, a different ionic liquid may be used, specifically one which has a wider electrochemical window, for instance, a tetraalkylammonium ionic liquid.

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Example 6: precipitation of fission products from [hmim]Cl using an organic solvent

Europium(III) chloride (EuCl_3) was used to simulate fission products dissolved in an ionic liquid. 4.66g [hmim]Cl and 1.05g EuCl_3 were dissolved in 20cm^3 dry acetonitrile. This solution was heated to 70°C under reflux in a dry dinitrogen atmosphere for 3 hours and allowed to cool. After approximately 30 minutes in a refrigerator, fine white crystals had precipitated. 1.81g of precipitate were collected. The results of elemental analysis of the crystals were 41.04% carbon, 6.86% hydrogen, and 9.22% nitrogen. The theoretical composition of the complex [hmim]₃[EuCl_6] ($\text{C}_{30}\text{Cl}_6\text{EuH}_{57}\text{N}_6$, RAM = 866.50 g mol^{-1}) is 41.58% carbon, 6.63% hydrogen and 9.70% nitrogen which suggests that this is the identity of the precipitate.

This Example shows that fission products dissolved within an ionic liquid can be recovered by the addition of an organic solvent.

CLAIMS

1. A method for separating a metal from a composition including said metal, the method comprising forming an electrolytic cell having an anode, a cathode and an electrolyte, the anode comprising a composition including said metal and the electrolyte comprising an ionic liquid, applying a sufficient potential difference
5 between the anode and the cathode to cause the metal to transfer from the anode to the cathode and be deposited thereon.
2. A method according to claim 1 wherein the cation component of the ionic liquid
10 is an organic cation.
3. A method according to claim 2 wherein the organic cation is N-substituted pyridinium, N,N'-disubstituted imidazolium, tetraalkylammonium or tetraalkylphosphonium.
15
4. A method according to claim 3 wherein the organic cation includes alkyl groups which are linear or branched and not all of the same chain length.
5. A method according to any of the preceding claims wherein the anion component
20 is halide, nitrate, sulphate, tetrafluoroborate, hexafluorophosphate or tetrachloroaluminate.
6. A method according to any claims 1 to 4 wherein the anion component is trifluoromethanesulfonate bis(trifluoromethanesulfonyl)imide.
25
7. A method according to any of the preceding claims wherein the ionic liquid is pre-loaded with metal ions.
8. A method according to claim 7 wherein the ionic liquid is pre-loaded with metal
30 ions by the addition of a soluble uranium salt.

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9. A method according to claim 7 wherein the ionic liquid is pre-loaded with uranium ions by displacement of a metal chloride.
- 5 10. A method according to claim 9 wherein the metal chloride is AgCl or CdCl₂.
11. A method according to claim 7 wherein the ionic liquid is pre-loaded with uranium ions by destructive reduction of the electrolyte.
- 10 12. A method according to any of the preceding claims wherein purified metal is deposited at the cathode.
13. A method according to any of the preceding claims wherein the metal is deposited at the cathode as a compound.
- 15 14. A method according to any of the preceding claims wherein the composition to be separated is irradiated nuclear fuel.
- 20 15. A method according to any of the preceding claims wherein the metal to be separated is uranium and/or plutonium.
16. A method according to any of the preceding claims wherein, after use in the method, the ionic liquid is purified for further use.
- 25 17. A process for the reprocessing of spent nuclear fuel, the process including a method of any preceding claim.
18. Use of an ionic liquid in the electrefining of a composition to separate a metal therefrom.
- 30 19. Use according to claim 18 wherein the composition is spent nuclear fuel.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number
WO 01/13379 A1

(51) International Patent Classification⁷: **G21C 19/48,**
C25C 1/22

BT9 5AG (GB). **ROONEY, David, William** [GB/GB],
Questor Centre, Queens University, David Keir Building,
Stanmillis Road, Belfast BT9 5AG (GB). **HEBDITCH,**
David [GB/GB]; BNFL Magnox Generation, Berkley,
Gloucestershire GL13 9PB (GB).

(21) International Application Number: PCT/GB00/03194

(22) International Filing Date: 18 August 2000 (18.08.2000)

(74) Agent: **HARRISON GODDARD FOOTE;** Tower
House, Merrion Way, Leeds LS2 8PA (GB).

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9919496.1 18 August 1999 (18.08.1999) GB

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE,
DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU,
ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,
LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO,
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,
TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(71) Applicant (*for all designated States except US*): **BRITISH
NUCLEAR FUELS PLC** [GB/GB]; Risley, Warrington,
Cheshire WA3 6AS (GB).

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **THIED, Robert,**
Charles [GB/GB]; British Nuclear Fuels Plc.-Research &
Technology, Sellafield Works, Seascale, Cumbria CA20
1PG (GB). **HATTER, Justine, Elisabeth** [GB/GB];
British Nuclear Fuels PLC, Risley, Warrington, Cheshire
WA3 6AS (GB). **SEDDON, Kenneth, Richard** [GB/GB];
Questor Centre, Queens University, David Keir Building,
Stanmillis Road, Belfast BT9 5AG (GB). **PITNER,**
William, Robert [GB/GB]; Questor Centre, Queens
University, David Keir Building, Stanmillis Road, Belfast

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette

(54) Title: PROCESS FOR SEPARATING METALS

(57) Abstract: A method for separating a metal from a composition including the metal involves forming an electrolytic cell in which the anode comprises a composition including the metal. The electrolyte is an ionic liquid. A sufficient potential difference is applied between the anode and the cathode to cause the metal to transfer from the anode to the cathode and to be deposited thereon.

Rec'd PCT/PTO
18 FEB 2002



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WO 01/13379

PCT/GB00/03194

Figure 1

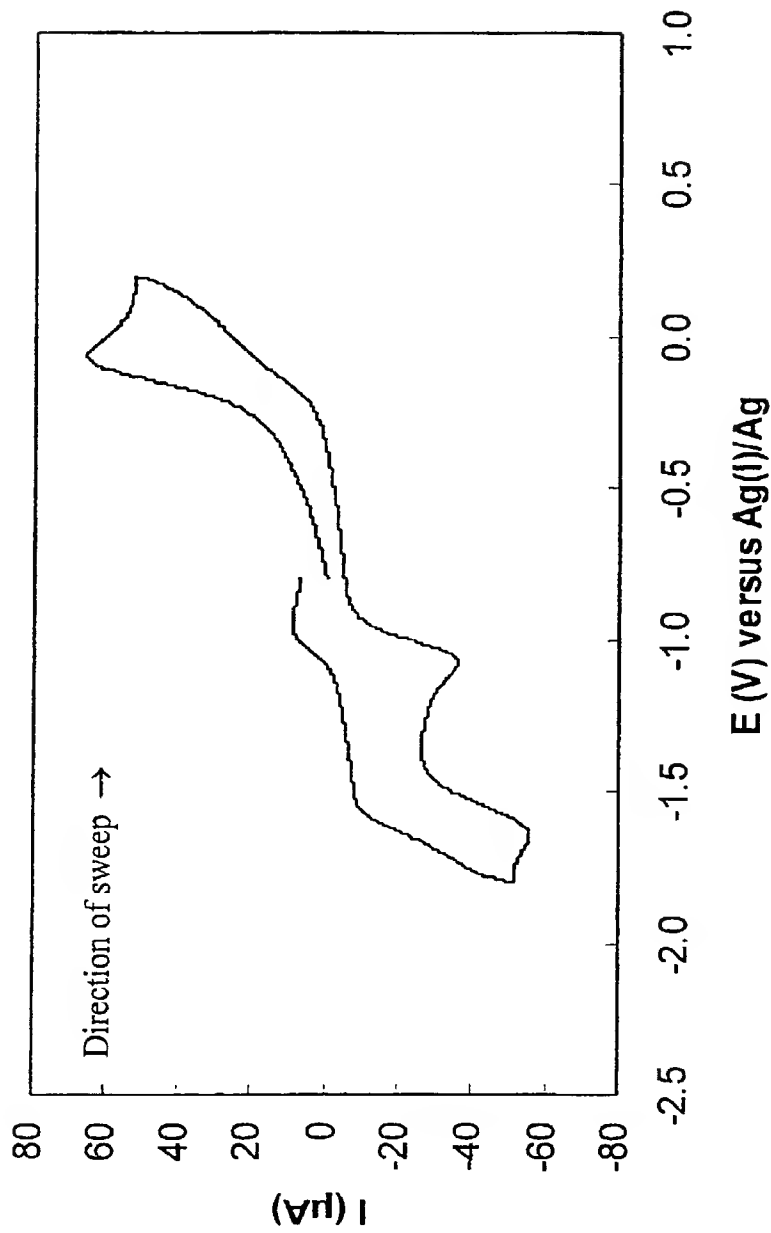
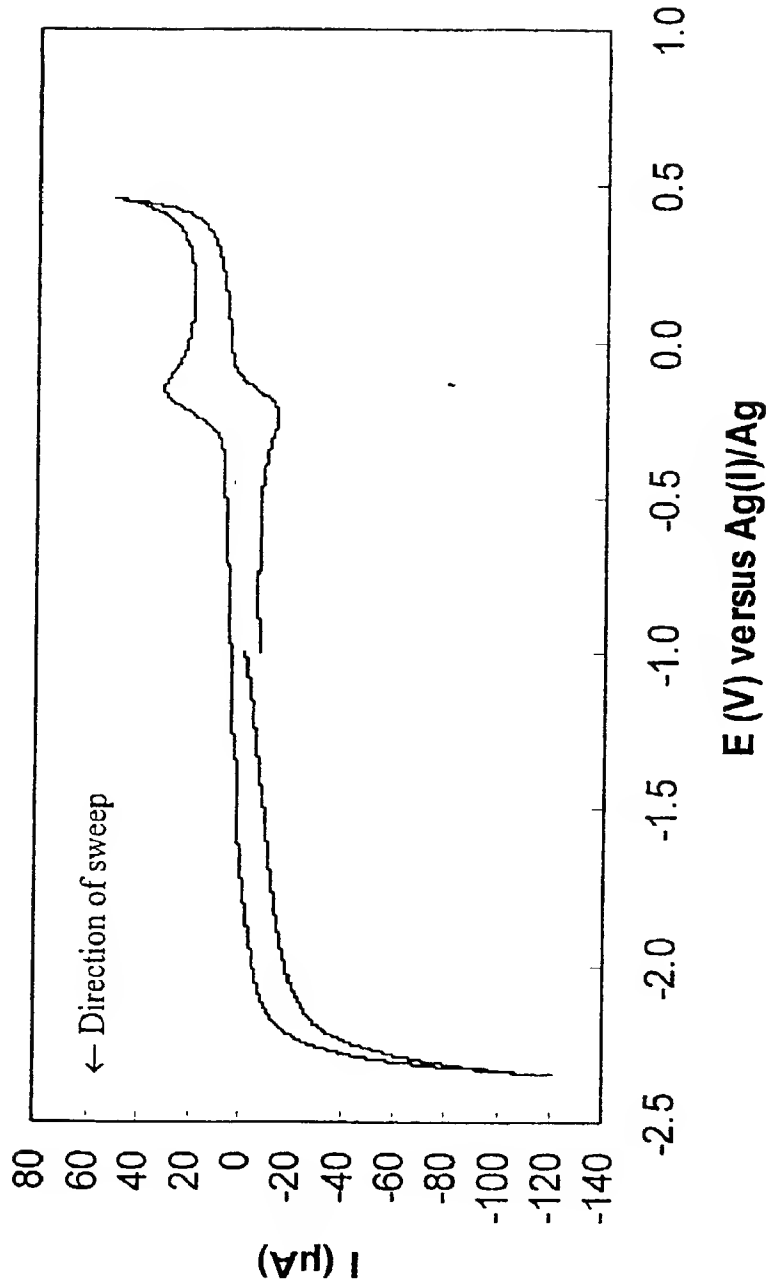


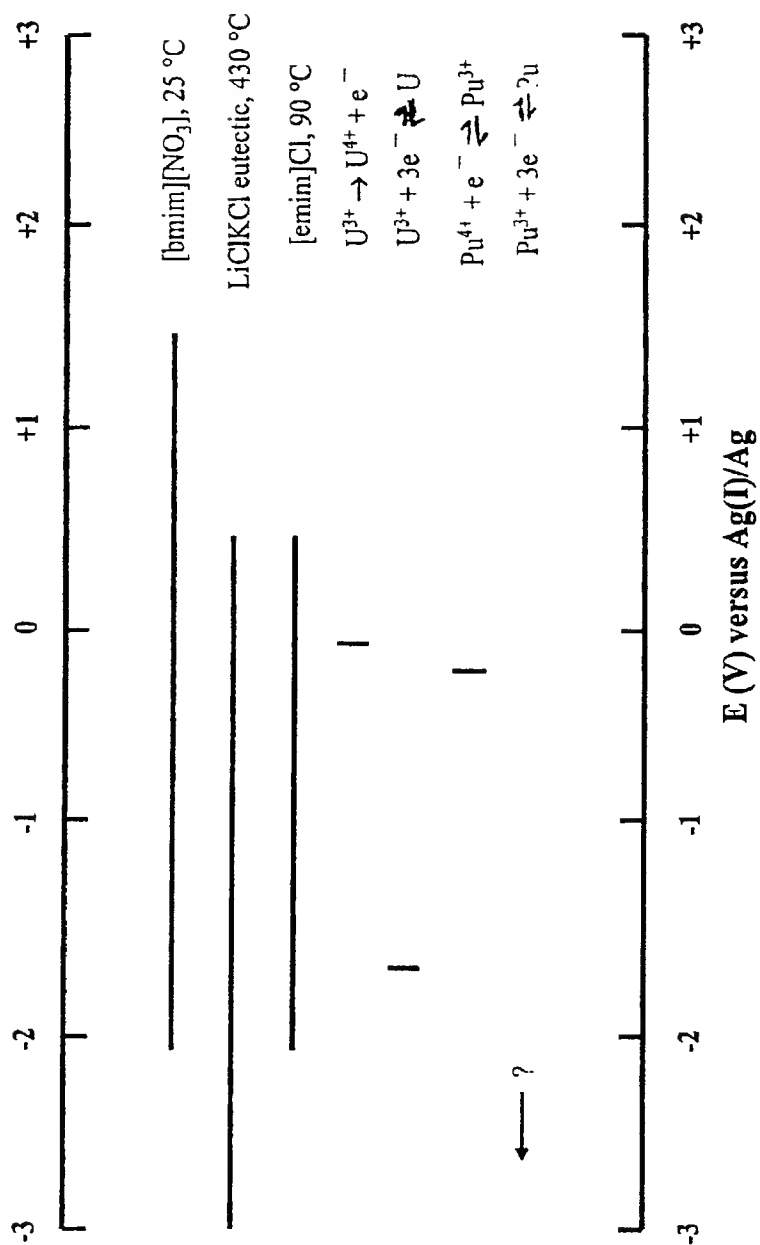
Figure 2



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Figure 3



DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

Attorney Docket No. 9052-106

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

the specification of which

☐ is attached hereto

OR

☒ was filed on February 18, 2002 as United States Application No. or PCT International Application Number (10/049,779) and was amended on _____ (if applicable). I hereby authorize and request Myers, Bigel, Sibley & Sajovec, P.A. to insert above in parenthesis the U.S. application number assigned to the application which claims priority in International Application No. PCT/GB00/03194 when known.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56, including material information that became available between the filing date of the prior application and the National or PCT International filing date of the continuation-in-part application, if applicable.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

PCT/GB00/03194	PCT	August 18, 2000	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
Number	Country	MM/DD/YYYY Filed	Priority Claimed
9919496.1	Great Britian	August 18, 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
Number	Country	MM/DD/YYYY Filed	Priority Claimed

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)
Application Number(s)	Filing Date (MM/DD/YYYY)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or § 365(c) of any PCT international application designating the United States of America, listed below.

Appln. Serial No.	Filing Date	Status Patented/Pending/Abandoned
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following registered attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. I also appoint the following registered attorney(s) to represent me before all competent International Authorities in connection with any and all international applications filed by me with an appropriate receiving office claiming priority to the U.S. application. I also appoint the following registered attorney(s) to make or receive payment on my behalf in connection with the filing of such international applications.

Customer Number:



20792

PATENT TRADEMARK OFFICE

Send correspondence to:

Customer Number:



20792

PATENT TRADEMARK OFFICE

Direct telephone calls to:

(919) 854-1400

Facsimile:

(919) 854-1401

Full name of (first/sole) inventor: 1-00 Robert Charles THIED

Inventor's

Signature: Robert Charles Thied Date: 23rd April 2002

Residence: SEASCALE, CUMBRIA, GREAT BRITAIN GBN

Citizenship: BRITISH

Mailing Address: SELLAFIELD WORKS, SEASCALE, CUMBRIA
LA20 1PG, GREAT BRITAIN

Full name of second inventor: \ Justine Elizabeth HATTER

Inventor's

Signature: _____ Date: _____

Residence:

Citizenship:

Mailing Address:

Customer Number:



20792

PATENT TRADEMARK OFFICE

Send correspondence to:

Customer Number:



20792

PATENT TRADEMARK OFFICE

Direct telephone calls to:

(919) 854-1400

Facsimile:

(919) 854-1401

Full name of (first/sole) inventor: Robert Charles THIED

Inventor's

Signature: _____ Date: _____

Residence:

Citizenship:

Mailing Address:

Full name of second inventor: 200 Justine Elizabeth HATTER

Inventor's

Signature: Justine Elizabeth Hatter Date: 30/4/2002

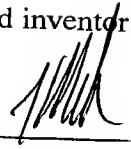
Residence: CHESHIRE, GREAT BRITAIN GBN

Citizenship: BRITISH

Mailing Address: RISLEY, WARRINGTON, CHESHIRE, WA3 6AS, GREAT BRITAIN

3-00
Full name of third inventor:Kenneth Richard SEDDON


Inventor's

Signature: Date: 22/5/02Residence: UKCitizenship: BRITISHMailing Address: SCHOOL OF CHEMISTRY, QUEEN'S UNIVERSITY
DAVID KEIR BUILDING
STRANHILL ROAD
BELFAST BT9 5AG, N. IRELAND GB5

Full name of fourth inventor:

4-00 William Robert PITNER

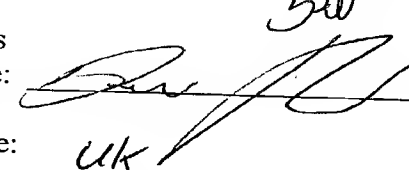
Inventor's

Signature: Date: 22/04/02Residence: UKCitizenship: USAMailing Address: School of Chemistry
Queen's University
Belfast BT9 5AG

Full name of fifth inventor:

5-00 David William ROONEY

Inventor's

Signature: Date: 7/5/02Residence: UKCitizenship: IRISH

Mailing Address:

SCHOOL OF CHEMICAL ENGINEERING
QUEEN'S UNIVERSITY BELFAST
BELFAST, BT9 5AG GB5

Full name of sixth inventor:

DAVID JOHN HEBDITCH
David HEBDITCH

Inventor's

Signature:

David John Hebditch

Date:

June 11, 2002

Residence:

GREENSIDE, BRADLEY GREEN, WOTTON-UNDER-
EDGE, GLOUCESTERSHIRE, ENGLAND GL12 7PL

Citizenship:

BRITISH

Mailing Address:

BNFLRUTHERFORD R201RISLEYWARRINGTONCHESHIREWA3 6ASCBH